Abstract: Methanol catalysis meets chemistry under confined conditions. Methanol is regarded as one of the most important future energy sources. ZnO/Cu composite materials are very effective in heterogeneous catalysis for methanol production due to the so-called strong metal–support interaction effect (SMSI). Therefore, materials of superior structural design potentially representing model systems for heterogeneous catalysis are highly desired. Ultimately, such materials could help to understand the interaction between copper and zinc oxide in more detail than currently possible. We report the preparation of nanocrystalline, size-selected ZnO inside the pore system of ordered mesoporous silica materials. A new, liquid precursor for ZnO is introduced. It is seen that the spatial confinement significantly influences the chemical properties of the precursor as well as determines a hierarchical architecture of the final ZnO/SiO₂ nanocomposites. Finally, the ability of the materials to act as model systems in methanol preparation is investigated. The materials are characterized by a variety of techniques including electron microscopy, X-ray scattering, solid-state NMR, EPR, EXAFS, and Raman spectroscopy, and physisorption analysis.

Introduction

At the birth of heterogeneous catalysis it was already realized that catalytic activity scales with surface area. Thus, maximum dispersity of particles is of extraordinary importance. Obviously, this makes the production of nanoscaled catalysts very tempting. Thus, the use of nanoparticles is not new to heterogeneous catalysis at all. Increasing capability of refined analytical techniques begins to enable deepened understanding of the relation between catalytic activity and the real structure of heterogeneous catalysts on a molecular scale. The use of this knowledge is highly desired in order to improve existing catalyst materials by addressing structure–property relationships. It was recently discussed by Schloegl et al. that in order to control and determine functional properties of a catalyst, it becomes necessary that the material possesses hierarchical design with structural features on multiple length scales ranging from the molecular to macroscopic domain. Thus, a synergism of refined analytical techniques and a refined materials synthesis is highly desired. To differentiate this refined approach to “classical” heterogeneous catalysis, Schloegl proposes the expression nanocatalysis.

Synthetic routes for the preparation of complex inorganic materials with hierarchical architecture still stand at the beginning. To develop a mode of operation bridging between multiple length scales (the meso approach) and inorganic materials synthesis is challenging. Such a materials preparation could, thus, be described as a “mesosynthesis” of materials. Application of this concept toward heterogeneous catalysis by inorganic particles means that besides nanosize the particles must be distributed in a hierarchical, spatial superstructure. In this respect, formation of inorganic nanoparticles inside the pores of nanoporous materials has been proven valuable. Mesoporous silica materials mostly of the MCM-41-type hosting polymers, noble metals, and semiconductors such as gallium nitride have been prepared successfully. Ideally the size and shape of those nanoparticles is determined by the pore size of the host matrix.

However, concerning catalysis and other applications, not only are metallic particles interesting but nanoscaled metal oxides are as well. Interestingly, little attention has, so far, been devoted toward the controlled preparation of metal–oxide nanoparticles under confinement of mesopores. Three problems occur: Low loading degrees, lack of crystallinity, and lack of control over particle size. Small pores (typically ca. 3 nm for MCM-type materials) and low concentration of oxide

(1) Bell, A. T. Science 2003, 299 (5613), 1688.